

What is claimed is:

1. A composite polymer electrolyte for a lithium secondary battery, which comprises:

a first polymer matrix made of a first porous polymer with a first pore size;

5 a second polymer matrix coated on the first polymer matrix and made of a single ion conductor, an inorganic material, and a second porous polymer with a second pore size smaller than the first pore size; and

10 an electrolyte solution impregnated into the first polymer matrix and the second polymer matrix.

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2. The composite polymer electrolyte of claim 1, wherein the first porous polymer is polyethylene, polypropylene, polyimide, polysulfone, polyurethane, polyvinylchloride, cellulose, nylon, polyacrylonitrile, polyvinylidene fluoride, polytetrafluoroethylene, a copolymer or blend thereof.

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3. The composite polymer electrolyte of claim 1, wherein the single ion conductor is perfluorinated ionomer, methylmethacrylate/alkaline metal methacrylate copolymer ionomer, methylmethacrylate/alkaline itaconate copolymer ionomer, methylmethacrylate/alkaline maleate copolymer ionomer, polystyrene ionomer, or a 20 blend thereof.

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4. The composite polymer electrolyte of claim 1, wherein the second porous polymer is a vinylidene fluoride based polymer, an acrylate based polymer, a copolymer or blend thereof.

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5. The composite polymer electrolyte of claim 4, wherein the second porous polymer is a copolymer of vinylidene fluoride and hexafluoropropylene, a copolymer of vinylidene fluoride and trifluoroethylene, a copolymer of vinylidene fluoride and tetrafluoroethylene, polymethylacrylate, polyethylacrylate, 30 polymethylmethacrylate, polyethylmethacrylate, polybutylacrylate, polybutylmethacrylate, polyvinylacetate, polyethylene oxide, polypropylene oxide, a copolymer or blend thereof.

6. The composite polymer electrolyte of claim 1, wherein the inorganic material is selected from the group consisting of silica, talc, alumina ( $Al_2O_3$ ),  $\gamma$ -LiAlO<sub>2</sub>, TiO<sub>2</sub>, zeolite, molybdenum phosphate hydrate, and tungsten phosphate hydrate.

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7. The composite polymer electrolyte of claim 1, wherein the inorganic material is added in an amount of 1 to 100% by weight, based on the total weight of the polymer of the second porous matrix.

10 8. The composite polymer electrolyte of claim 1, wherein the first polymer matrix has a thickness of 10 to 25  $\mu m$  and the second polymer matrix has a thickness of 0.5 to 10  $\mu m$ .

15 9. The composite polymer electrolyte of claim 1, wherein the electrolyte solution is made of ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, methylethyl carbonate, tetrahydrofuran, 2-methyltetrahydrofuran, dimethoxyethane, methyl formate, ethyl formate, gamma-butyrolactone, or a mixture thereof.

20 10. The composite polymer electrolyte of claim 1, wherein the electrolyte solution is impregnated into the first polymer matrix and the second polymer matrix in an amount of 1 to 1,000% by weight, based on the total weight of the polymer of the first polymer matrix and the second polymer matrix.

25 11. The composite polymer electrolyte of claim 1, wherein the electrolyte solution comprises at least one lithium salt selected from the group consisting of lithium perchlorate ( $LiClO_4$ ), lithium triflate ( $LiCF_3SO_3$ ), lithium hexafluorophosphate ( $LiPF_6$ ), lithium tetrafluoroborate ( $LiBF_4$ ), and lithium trifluoromethanesulfonylimide ( $LiN(CF_3SO_2)_2$ ).

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12. The composite polymer electrolyte of claim 11, wherein the lithium salt is dissolved in the electrolyte solution in an amount of 1 to 200% by weight, based on the total weight of the polymer of the first polymer matrix and the second polymer matrix.

13. A method of manufacturing a composite polymer electrolyte for a lithium secondary battery, the method comprising:

5 preparing a first polymer matrix made of a first porous polymer with a first pore size;

uniformly dissolving a single ion conductor, an inorganic material, and a second porous polymer with a second pore size smaller than the first pore size in a co-solvent in a predetermined ratio to produce a solution;

10 coating the first polymer matrix with the solution to form a second polymer matrix on the first polymer matrix; and

impregnating the first polymer matrix and the second polymer matrix with an electrolyte solution.

14. The method of claim 13, wherein the co-solvent is selected from the 15 group consisting of ethanol, methanol, isopropyl alcohol, acetone, dimethylformamide, dimethylsulfoxide, N-methylpyrrolidone, and a mixture thereof.